
Molecular Mechanics (MM4) Vibrational Frequency Calculations for Alkenes and Conjugated Hydrocarbons*

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ABSTRACT

Vibrational frequencies for 11 alkenes and 8 conjugated hydrocarbons have been analyzed with MM4. The root mean square (rms) difference between the experimental and MM4 values is 25 cm^{-1} for seven alkenes and 31 cm^{-1} for eight conjugated hydrocarbons, compared to MM3 rms differences of 38 cm^{-1} for alkenes and 52 cm^{-1} for conjugated hydrocarbons. New MM4 cross-terms which primarily affect vibrational frequencies include bend-torsion-bend, improper torsion-torsion-improper torsion, and stretch-stretch, which improve in-plane bending, out-of-plane bending, and stretching frequencies, respectively. The stretching force parameter for conjugated bonds has been changed to vary quadratically with bond order (instead of linearly, as in MM3). The addition of a V4 term to the torsional potential for alkenes and conjugated hydrocarbons helps improve torsional frequencies. The torsion-torsion cross-term increases out-of-plane bending frequencies in conjugated hydrocarbons. This overall improvement in the vibrational frequencies does not result in any sacrifice in the accuracy of other quantities calculated by MM4. © 1996 by John Wiley & Sons, Inc.

Introduction

The MM3 force field¹ gave creditable results for the structures, energies, vibrational spectra, and other properties of alkanes, alkenes, and functionalized organic molecules. The most serious

discrepancies between calculation and experiment were found in the vibrational frequencies, but there were also significant errors in some of the other properties. After extensive studies to determine how these errors might be reduced, the MM4 force field was devised. Other articles in this series have discussed this force field for alkanes,² alkenes,³ and conjugated hydrocarbons.^{4,5} The fitting of vibrational spectra was an important part of the formulation of the force field, as described in these articles. For the most part, however, this topic was postponed in those articles. It is discussed here in

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detail for alkenes and conjugated hydrocarbons. Although there are some significant improvements for conformational energy barriers and differences and smaller ones for heats of formation and geometries for hydrocarbons with MM4, the vibrational frequencies show the most improvement. This was accomplished, in part, with the addition of the new cross-terms mentioned earlier and elaborated on here. These terms provide the explicit off-diagonal contributions to the force constant (F) matrix, to which the vibrational frequencies are most sensitive. The alkane vibrational frequencies have been improved by MM4: The rms error for a test set of alkanes is 36 cm^{-1} for MM3¹ but is lowered to 25 cm^{-1} with MM4.² A similar improvement has been achieved for alkenes, from 38 cm^{-1} (MM3⁶) to 25 cm^{-1} . Likewise, the MM4 rms error for conjugated hydrocarbons has also been reduced compared to MM3⁷ (from 52 to 31 cm^{-1}).

Experimental vibrational frequencies are listed in the tables as indicated, along with MM3 and MM4 calculated comparisons for ethylene (Table III), propene (Table IV), isobutene (Table VIII), skew-1-butene (Table IX), *cis*-2-butene (Table XIII), *trans*-2-butene (Table XIV), *trans*-butadiene (Table XVII), *cis*-butadiene (Table XVIII), etc. Additional tables are given in the Supplemental Material for *cis*-1-butene (Table X), *cis*- and *gauche*-3-methyl-1-butene (Tables XI and XII), 1,4-cyclohexadiene (Table XV), cyclopentene (Table XVI), *trans*- and *gauche*-isoprene (Tables XIX and XX), toluene (Table XXI), and cyclopentadiene (Table XXII). Summaries of these results, including the rms difference and the largest frequency error for each compound, are listed in Tables XXIII and XXIV.

It is important to note that the resources were available to us to calculate vibrational frequencies at the HF/6-31G** level if necessary to further analyze questionable frequency assignments. This was not so when the MM3 force field was developed.

The additional off-diagonal cross-terms incorporated into MM4 provide a more accurate description of the true force field. The new force parameters allow for better separations of the vibrational modes that are coupled together. The equations were discussed in the alkenes article,³ and the effects of the cross-terms on the vibrational frequencies are elaborated on in this article. Groups of similar frequencies (i.e., bending, torsional, or stretching) are presented in tables in the appropriate following sections in order to demonstrate more clearly the nature of the improvements which re-

sult from particular cross-terms. These will be taken up, in turn, as following.

Bend-torsion-bend

The C_{sp^2} -H bending vibrational frequencies are calculated poorly by MM3.⁶ The addition of a bend-torsion-bend (btb) term for the $X-C_{sp^2}-C_{sp^2}-Y$ torsion (see Table I) greatly improves the in-plane bending frequencies for a number of alkenes and conjugated hydrocarbons, with rms error reduction from 58 cm^{-1} (MM3) to 28 cm^{-1} (MM4) for the set of vibrational frequencies in Table I. A particularly clear example of this cross-term's effect is shown for ethylene. The ethylene B_{1g} and B_{2u} rocking frequencies are calculated too low and high, respectively, by MM3. Adjusting the bending force constant can only lower or raise both at the same time. The btb term raises the asymmetric B_{1g} rock while at the same time lowering the symmetric B_{2u} rock. Similar in-plane bending frequencies in other molecules are also improved by this term.

Improper Torsion-Torsion-Improper Torsion

Two out-of-plane bending frequencies of ethylene with B_{1u} and B_{2g} symmetries (frequencies 10 and 11 in Table III) would each be calculated with an error of about 60 cm^{-1} by MM3 if the errors for these frequencies were averaged out. The improper torsion-torsion-improper torsion term increases the symmetric B_{1u} out-of-plane bending frequency while also reducing the asymmetric B_{2g} frequency, which is calculated too high without this correction (see Table II).

V4 Term Addition to Torsional Potential

As mentioned in the alkenes article,³ the V4 term allows torsional frequencies to be calculated more accurately while also fitting the planar versus pyramidal transition states of alkenes better than was possible with MM3. For instance, the ethylene A_u torsional frequency is now fit better with MM4 than MM3, since it can be reduced with the V4 term without lowering V2 (see Table III). For the conjugated hydrocarbons, the V1, V2, V3, and V4 terms all affect the torsional and out-of-

TABLE I.
C_{sp²}—H In-Plane Bending Frequencies (cm⁻¹).

Compound	Sym.	Mode	Exp. ^a	MM3	Δ	Max. Δ	MM4	Δ	Max. Δ
Ethylene	B _{3u}	CH ₂ scissors	1444	1449	+5		1443	-1	
	A _g	CH ₂ scissors	1342	1227	-115	-115	1327	-15	
	B _{1g}	CH ₂ rock	1222	1111	-111		1181	-41	-41
	B _{2u}	CH ₂ rock	826	923	+97		837	+11	
Propene	A'	CH ₂ bend	1420	1441	+21		1422	+2	
	A'	CH bend	1298	1226	-72	-72	1295	-3	-3
	A'	CH ₂ rock	1174	1131	-43		1177	+3	
Isobutene	A ₁	CH ₂ bend	1416	1428	+12	+12	1411	-5	
	B ₁	CH ₂ rock	1282	1273	-9		1273	-9	-9
c-2-Butene	B ₁	CH rock	1422	1441	+19	+19	1484	+62	+62
	A ₁	CH rock	1267	1270	+3		1273	+6	
t-2-Butene	B _u	CH rock	1306	1345	+39		1344	+35	+35
	A _g	CH rock	1309	1230	-79	-79	1312	+3	
Benzene	A _{2g}	CH in-pl. bend	1350	1368	+18		1398	+48	
	E _{2g}	CH in-pl. bend	1178	1185	+7		1163	-15	
	B _{2u}	CH trig. bend	1146	1259	+105	+105	1208	+62	+62
	E _{1u}	CH in-pl. bend	1037	982	-55		1031	-6	
t-Butadiene	A _g	CH ₂ scissors	1442	1474	+32		1462	+20	
	A _g	CH rock	1291	1213	-78	-78	1305	+14	
	A _g	CH ₂ rock	890	883	-7		859	-31	
	B _u	CH ₂ scissors	1385	1396	+11		1409	+24	
	B _u	CH rock	1296	1253	-43		1337	+41	+41
	B _u	CH ₂ rock	991	1033	+42		1014	+23	
	rms				57.5			28.0	
	ave.				-8.8			+9.9	
max. error						-115			+62

^a All results are gas phase unless stated otherwise.

plane bending frequencies. Both sets of frequencies have been somewhat improved by MM4, although the out-of-plane bending frequencies for benzene (and to a lesser extent toluene) are still too low overall (see Tables VI and XXI). Improving these frequencies would come at the expense of rotational barriers and heats of formation involving conjugated compounds. Also, the fact that alkene out-of-plane bending frequencies are mostly too high while the conjugated ones are mainly too low suggests a bond order/bending constant relationship which is not explicitly taken into account in MM4.

Stretch-Bend

The stretch-bend constant of X—C_{sp²}—H used in MM4 is now 0.20 mdyne/rad, a value twice as large as that needed for X—C_{sp³}—H. If the X—C_{sp³}—H value of 0.10 were used as the X—C_{sp²}—H stretch-bend constant, the C=C

stretching and some CH bending frequencies would be calculated too high and low, respectively. For example, the ethylene C=C stretching and CH₂ scissoring (A_g symmetry) frequencies would have to be averaged out with errors from experiment of about 50 cm⁻¹ for both frequencies (see frequencies 5 and 7 in Table 3), while the MM4 error is only about 10 cm⁻¹ for these frequencies.

Another example is the propene CH bend frequency (frequency number 12 in Table IV), which is calculated by MM3 to be 72 cm⁻¹ lower than experiment, but by MM4 to be only 3 cm⁻¹ lower.

Bond Order Dependence for Stretching Parameters Involving Conjugation

The C_{sp²}=C_{sp²} stretching frequencies of alkenes are calculated well with MM3, but conjugated C_{sp²}

TABLE II.
Torsional and Out-of-Plane Bending Frequencies (cm⁻¹).

Compound	Sym.	Mode	Exp. ^a	MM3	Δ	Max. Δ	MM4	Δ	Max. Δ
Ethylene	A _u	C = C tors.	1023	1089	+66		1026	+3	
	B _{2g}	oop bend	943	931	-18		967	+24	+24
	B _{1u}	oop bend	949	1067	+124	+124	947	-2	
Propene	A''	CH ₂ twist	990	982	-8		999	+9	
	A''	CH ₂ wag	912	947	+35	+35	954	+42	+42
	A''	C = C tors.	575	588	+13		592	+17	
Isobutene	B ₂	CH ₂ twist	890	936	+46	+46	953	+63	+63
	A ₂	CH ₂ wag	697	717	+20		727	+30	
	B ₂	sym. def.	429	421	-8		441	+12	
c-2-Butene	A ₂	CH wag	1044	1101	+57	+57	1066	+22	
	B ₂	CH wag	685	726	+41		733	+48	+48
	A ₂	sym. def.	402	422	+20		429	+27	
t-2-Butene	A _u	CH wag	975	957	-18		995	+20	
	B _g	CH wag	750	810	+64	+64	779	+29	+29
	A _u	sym. def.	240	239	-1		250	+10	
Benzene	B _{2g}	CH oop	990	1119	+129	+129	968	-22	
	E _{1g}	CH oop	846	773	-73		816	-30	
	A _{2u}	CH oop	674	569	-105		686	+12	
	E _{2u}	CH oop	967	1030	+63		950	-17	
	B _{2g}	CCC oop	707	581	-126		624	-83	-83
t-Butadiene	E _{2u}	CCC oop	399	361	-38		388	-11	
	A _u	CH wag	1013	1101	+88		1000	-13	
	A _u	CH ₂ wag	908	955	+47		930	+22	
	A _u	CH ₂ twist	524	508	-16		532	+8	
	A _u	C — C tor	163	164	+1		148	-15	
t-Isoprene	B _g	CH wag	967	1090	+123	+123	943	-24	
	B _g	CH ₂ wag	911	956	+45		930	+19	
	B _g	CH ₂ twist	753	661	-92		692	-61	-61
	A''	CH wag	990	1084	+94	+94	966	-24	
	A''	=CH ₂ wag	903	957	+54		927	+24	
	A''	=CH ₂ wag	891	917	+26		921	+30	
	A''	=CH ₂ twist	755	686	-69		709	-46	-46
	A''	=CH ₂ twist	622	615	-7		628	+6	
	A''	C — CH ₃ wag	412	366	-46		414	+2	
	A''	C — C tors.	153	95	-58		115	-38	
	rms				64.7			29.9	
	ave				13.5			0.9	
max. error					+129				-83

^a All results are gas phase unless stated otherwise.

—C_{sp²} stretches are calculated to be systematically too high. In MM3, the stretching force parameter, K_s , has a linear relationship to the bond order P_{ij} , as indicated in eq. (1), where $K_s(1)$ is the stretching force parameter for a P_i bond order of 1, and t is the slope of the K_s bond order dependence.

$$K_s(P_{ij}) = K_s(1) - t(1 - P_{ij}) \quad (1)$$

Similarly, the natural bond length, l_0 has a linear relationship to bond order, as evidenced in eq. (2), where $l_0(1)$ is the natural bond length with a bond

order of 1 and s is the slope of the l_0 bond order dependence.

$$l_0(P_{ij}) = l_0(1) + s(1 - P_{ij}) \quad (2)$$

Previous studies indicate that eq. (2) is correct.¹⁰ In the harmonic approximation, bond length is proportional to the square root of the force constant [see eq. (3)], where l_0 is the natural bond length and c and d are constants.

$$l_0 = c - d^* \sqrt{K_s} \quad (3)$$

TABLE III.
Ethylene.

	Sym.	Mode	Exp. ⁸	MM3	Δ	MM4	Δ
1	B _{2u}	CH str.	3106	3107	+1	3107	+1
2	B _{1g}	"	3103	3103	0	3089	-14
3	A _g	"	3026	3023	-3	3039	+13
4	B _{3u}	"	2989	2995	+6	3007	+18
5	A _g	C=C str.	1623	1596	-27	1618	-5
6	B _{3u}	CH ₂ sci.	1444	1449	+5	1443	-1
7	A _g	"	1342	1227	-115	1327	-15
8	B _{1g}	CH ₂ rock	1222	1111	-111	1181	-41
9	A _u	C=C tors.	1023	1089	+66	1026	+3
10	B _{1u}	oop. bend	949	931	-18	947	-2
11	B _{2g}	oop. bend	943	1067	+124	967	+24
12	B _{2u}	CH ₂ rock	826	923	+97	837	+11
				rms	68.2		16.7
				max.	+124		-41

Substituting eq. (3) into eq. (2) leads to the result shown in eq. (4).

$$K_s(P_{ij}) = d^{-2}[(l_0 - c) + s(1 - P_{ij})]^2 \quad (4)$$

Expanding eq. (4) gives eq. (5).

$$K_s(P_{ij}) = P_{ij}^2 + aP_{ij} + b \quad (5)$$

TABLE IV.
Propene.

	Sym.	Mode	Exp. ⁸	Exp. ⁹	MM3	Δ	MM4	Δ
1	A'	CH ₂ asym. str.	3091	3090	3107	+16	3100	+9
2	A'	CH str.	3022(R)	3036	3040	+18	3040	+18
3	A'	CH ₂ sym. str.	3008(R)	2992	3009	+1	3017	+9
4	A'	CH ₃ asym. str.	2973	2993	2972	-1	2976	+3
5	A''	CH ₃ asym. str.	2953	2954	2970	+17	2972	+19
6	A'	CH ₃ sym. str.	2932	2870	2879	-53	2881	-51
7	A'	C=C str.	1656	1652	1667	+11	1661	+5
8	A'	CH ₃ def.	1459	1474	1478	+19	1454	-5
9	A''	CH ₃ def.	1443	1443	1444	+1	1438	-5
10	A'	CH ₂ bend	1420(R)	1419	1441	+21	1422	+2
11	A'	CH ₃ def.	1378	1378	1365	-13	1380	+2
12	A'	CH bend	1298	1298	1226	-72	1295	-3
13	A'	CH ₂ rock	1174	1229	1131	-43	1178	+4
14	A''	CH ₃ rock	1045	1045	1101	+56	1058	+13
15	A''	C=C tors. twist	990	991	982	-8	999	+9
16	A'	CH ₃ rock	(935)	1172	955	+20	961	+26
17	A'	C-C str.	(919)	920	922	+3	910	-9
18	A''	CH ₂ wag	912	912	947	+35	954	+42
19	A''	CH ₂ tors. twist	575	578	588	+13	592	+17
20	A'	C=C—C	428	428	424	-4	427	-1
21	A''	CH ₃ tors.	188	174	183	-5	194	+6
				rms		28.3		17.8
				max.		-72		-51

The value of a is small, and if we omit the term aP_{ij} in eq. (5), we arrive at an equation similar to eq. (1) as shown in eq. (6). However, the relationship involves P_{ij}^2 rather than P_{ij} .

$$K_s(P_{ij}) = K(1) - t(1 - P_{ij}^2) \quad (6)$$

The values for $K_s(P_{ij})$ are plotted against P_{ij} in Figure 1. Equation (6) is used in the MM4 program, and thus the $C_{sp^2} = C_{sp^2}$ stretching frequencies are calculated better compared with experiment by MM4 than by MM3, as shown in Table V.

Stretch-Stretch

MM3 benzene stretching frequencies are calculated poorly, especially the B_{2u} stretch (see Tables V and VI). It was decided when MM3 was parameterized to fit to the Pitzer and Scott value,¹¹ where the B_{2u} frequency was assigned at 1657 cm⁻¹. At the time, this was the only way evident to fit the experimental C—C stretching frequencies within a reasonable error limit. However, later it was decided that a stretch-stretch cross-term might be

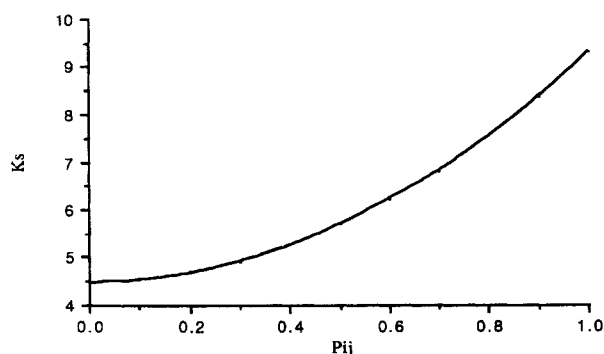


FIGURE 1. Bond order (P_{ij}) vs. stretching force constant (K_s).

used to better calculate these frequencies. The inclusion of this term in MM4 resulted in frequencies that are more in line with the results of Varsanyi and Szoke¹³ (particularly the B_{2u} at 1309 cm^{-1}) and with *ab initio* calculations.¹²

The addition of the stretch-stretch term helps reduce the overall MM4 stretching frequency devi-

ations from experiment. Benzene has coupled stretching frequencies, including E_{2g} of 1599 cm^{-1} , E_{1u} of 1482 cm^{-1} , B_{2u} of 1309 cm^{-1} , and A_{1g} of 993 cm^{-1} . In MM3, the latter two stretches are calculated too far apart (using the current assignments); B_{2u} is 1657 cm^{-1} (+348) and A_{1g} is 911 cm^{-1} (-81). The E_{2g} and E_{1u} stretches are calculated acceptably by MM3 with values of 1637 cm^{-1} (+38) and 1482 cm^{-1} (0). The stretch-stretch term improves the B_{2u}/A_{1g} gap in benzene but worsens somewhat the benzene E_{2g}/E_{1u} and isobutene B_1/A_1 stretching differences (see Tables V and VI).

Styrene is also affected by this term. The largest discrepancies between MM4 and experiment occur in styrene for aryl C—C stretches 10 and 17 (see Table VII). Data derived from the scaled quantum mechanical force field method (SQM)¹⁴ and infrared (IR) experiments by Condirston and Laposa (CL)¹⁵ and Marchand and Quinard (MQ)¹⁶ are presented in this table. Both styrene and benzene show stretching couplings, and a stretch-stretch-cross-term might further improve the current errors for the stretches in these compounds.

TABLE V.
CC Stretching Frequencies (cm^{-1}).

Compound	Sym.	Exp. ^a	MM3	Δ	Max. Δ	MM4	Δ	Max. Δ
Ethylene	A_g	1623	1596	-27	-27	1618	-5	-5
Propene	A'	1656	1667	+11	+11	1661	+5	
	A'	919	922	+3		910	-9	-9
Isobutene	A_1	1661	1628	-33		1679	+18	
	B_1	974	935	-39		928	-46	-46
	A_1	807	852	+45	+45	843	+36	
c-2-Butene	A_1	1669	1714	+45	+45	1691	+22	+22
	B_1	978	962	-16		979	+1	
	A_1	881	862	-19		881	0	
t-2-Butene	A_g	1680	1734	+54		1703	+23	
	B_u	1069	1133	+64	+64	1067	-2	
	A_g	864	887	+21		899	+33	+33
Benzene	A_{1g}	993	911	-82		1020	+27	
	B_{2u}	1309	1657	+348	+348	1379	+70	+70
	E_{1u}	1482	1482	0		1508	+26	
	E_{2g}	1599	1637	+38		1534	-65	
t-Butadien	A_g	1643	1701	+58	+58	1633	-10	
	A_g	1205	1185	-20		1195	-10	-10
	B_u	1599	1569	-28		1591	-8	
	rms			38.2 ^b / 88.7 ^c			32.1	
	ave.			+5.2 ^b / +22.3 ^c			+3.1	
max. error					+348			+70

^a All results are gas phase unless stated otherwise.

^b Without benzene B_{2u} frequency.

^c With benzene B_{2u} frequency.

TABLE VI.
Benzene.^a

Sym.	Mode	Exp. ¹³	Exp. ¹¹	MM3	Δ^b	MM4	Δ^b
A _{1g}	C—H str. in phase	3070	3062	3058	-12	3066	-4
	Breathing	993	993	911	-82	1020	+27
A _{2g}	C—H in-plane bend	1350	1298	1368	+18	1398	+48
B _{2g}	C—H oop trig.	990	1016	1119	+129	968	-22
	C—C—C oop bend	707	685	581	-126	624	-83
E _{2g}	C—H stretch	3056	3048	3043	-13	3037	-19
	C-C stretch	1599	1595	1637	+38	1534	-65
	C-H in-plane bend	1178	1178	1185	+7	1164	-14
	C-C-C in-plane bend	608	606	596	-12	601	-7
E _{1g}	C-H oop. bend	846	850	773	-73	816	-30
A _{2u}	C-H oop. in phase	674	671	569	-105	686	+12
B _{1u}	C-H trig. stretch	3057	3060	3038	-19	3031	-26
	C—C—C trig. bend	1010	1010	947	-63	1023	+13
B _{2u}	C—C stretch	1309	1693	1657	+348	1379	+70
	C-H trig. bend	1146	1170	1249	+103	1208	+62
E _{2u}	C-H oop. bend	967	985	1030	+63	950	-17
	C—C—C oop. bend	399	400	361	-38	388	-11
E _{1u}	C—H stretch	3064	3080	3051	-13	3054	-10
	C-C stretch	1482	1485	1482	0	1508	+26
	C-H in pl. bend	1037	1035	982	-55	1032	-5
	rms				57.9 ^c		33.6
	max.				+129 ^c		-83

^a All results are gas phase unless stated otherwise.^b The MM results are compared to those in ref. 13.^c These values are calculated without the B_{2u} C—C stretching frequency (with this B_{2u} frequency, the rms / max. are 85.3 / +348 cm⁻¹).

The in- and out-of-plane aryl-H bending modes have been significantly improved with MM4 due to the bend-torsion-bend and improper torsion-torsion-improper torsion torsion cross-terms. Styrene was not included explicitly in the parameterization process for MM3 or MM4.

Isobutene

Isobutene has a B₁ asymmetric stretch at 974 cm⁻¹ and an A₁ symmetric stretch at 807 cm⁻¹ (frequencies 29 and 9 in Table VIII). An increase in the stretch-stretch term causes the B₁ and A₁ stretches to decrease and increase, respectively. Since MM3 already calculates the B₁ stretch too low and the A₁ too high, the increase in this term required to improve the benzene stretching frequencies optimally will worsen those of isobutene. Therefore, as detailed in a previous article,³ the stretch-stretch parameter (K_{ss}) for C_{sp³}—C_{sp²}—X was assigned a value one half that of C_{sp²}—C_{sp²}—X.

cis- and skew-1-Butene and 3-Methyl-1-Butene Vibrational Frequencies

Two CH₃ rocking frequencies in *cis*-1-butene (see frequencies 18 and 19 in Table IX) are calculated poorly by MM3 and MM4 compared with experiment. Since comparable CH₂ rocks for propene and isobutene were assigned to much higher frequencies by MM than by the infrared experiments of Barnes and Howell,⁹ *ab initio* calculations at the HF/6-31G** level were carried out on *cis*- and *skew*-1-butene for comparison.[‡] The *ab initio* frequencies have been scaled down by 10% and are shown next to the experimental results in Tables IX and X (the latter in Supplementary Material). For the frequencies in question, the *ab initio* results for *cis*- and *gauche*-1-butene are closer to

[‡] All *ab initio* calculations were carried out with optimization at the 6-31G*/MP2 level in the present work, using the Gaussian92 program (ref. 33) unless otherwise stated.

TABLE VII.
Styrene.^a

	Mode	SQM ¹⁴	CL ¹⁵	MQ ¹⁶	MM3	Δ^b	MM4	Δ^b
	In-plane							
1	CH ₂ stretching	3113	3105	3080	3121	+16	3113	+8
2	C*H stretching	3089	3090	3060	3072	-18	3066	-24
3	C*H stretching	3080	3084	—	3055	-29	3058	-26
4	C*H stretching	3068	3061	—	3049	-12	3047	-14
5	C*H stretching	3057	3055R	—	3043	-12	3036	-19
6	C*H stretching	3050	3029	3028	3040	+11	3032	+3
7	CH ₂ stretching	3045	3010	3010	3034	+24	3036	+26
8	CH stretching	3030	2982	2980	3106	+34	3001	+19
9	C=C stretching	1639	1630	1631	1703	+73	1639	+9
10	C*C* stretching	1612	1601	1602	1661	+60	1544	-57
11	C*C* stretching	1585	1575	1577	1639	+64	1538	-37
12	Aryl-H rocking	1499	1494	1497	1605	+111	1520	+26
13	Aryl-H rocking	1457	1450	1450	1515	+65	1494	+44
14	CH ₂ scissoring	1432	1412	1415	1486	+74	1454	+42
15	Aryl-H rocking	1344	1334	1337	1437	+100	1390	+56
16	CH rocking	1312	1303R	1317	1268	-35	1336	+34
17	C*C* stretching	1272	1289	1290	1367	+78	1375	+86
18	C—C* stretching	1204	1202	1208	1234	+32	1205	+3
19	Aryl-H rocking	1190	1182	1180	1219	+37	1188	+6
20	Aryl-H rocking	1168	1155	1156	1176	+21	1183	+28
21	C*C* stretching	1089	1083	1083	1063	-20	1096	+13
22	C*C* stretching	1037	1032	1032R	1033	+1	1051	+19
23	C*C* stretching	1022	1019	1021	972	-47	1032	+13
24	Ring def.	998	999R	1001R	929	-70	1010	+11
25	Ring def.	770	776	774R	738	-38	791	+15
26	Ring def.	622	623	647R	607	-16	610	-13
27	Skeletal def.	548	554	615	559	+5	559	+5
28	Skeletal def.	439	442R	438	428	-14	443	+1
29	Subst. def.	231	241R	237	279	+38	268	+27
	Out-of-plane							
30	CH ₃ twisting	1003	992	990	1071	+79	955	-37
31	Aryl-H wagging	984	983	988R	1098	+115	964	-19
32	Aryl-H wagging	965		980	1022	+42	950	-30
33	CH ₂ wagging	932	909	905	962	+53	936	+27
34	Aryl-H wagging	909	909	905R	917	+8	896	-13
35	Aryl-H wagging	831	841	840	762	-79	817	-24
36	Aryl-H wagging	771	776	775	699	-77	748	-28
37	Ring def.	684	698	695	596	-102	667	-31
38	Ring def.	627	640R	553	552	-88	593	-47
39	Ring def.	426	434	450	389	-45	423	-11
40	Ring def.	397	407R	400	360	-47	384	-23
41	Skeletal def.	193	212R	214	186	-26	186	-26
42	C*—C	(43)			31	—	(45)	—
	rms					55.7		29.6
	max.					+115		+86

^a All results are gas phase unless stated otherwise.^b MM results compared to ref. 15, except frequency 32, which is compared with ref. 16.

TABLE VIII.
Isobutene.^a

	Sym.	Mode	Exp. ^b	Exp. ⁹	MM3	Δ^b	MM4	Δ^b
1	A1	CH ₂ str.	2980	3019(B2)	3013	+33	3027	+47
2		CH ₃ asym. str.	2941	2942	2973	+32	2978	+37
3		CH ₃ sym. str.	2912	2884	2880	-32	2883	-29
4		C=C str.	1661	1665	1628	-33	1679	+18
5		CH ₃ asym. def.	1470	1442	1467	-3	1466	-4
6		CH ₂ rock	1416	1416	1428	+12	1412	-4
7		CH ₃ sym. def.	1381	1377	1338	-43	1374	-7
8		CH ₃ rock	1064	1053	947	-117	1045	-19
9		C—C str.	807	802	852	+45	843	+36
10	A2	C=C—C bend	387	(378)	380	-7	371	-18
11		CH ₃ asym. str.	—	(2950)	2971	+21	2974	+24
12		CH ₃ asym. def.	—	(1450)	1446	-4	1440	-10
13		CH ₃ rock	971	988	929	-42	995	+24
14		CH ₂ wag	697	700	717	+20	727	+30
15	B2	CH ₃ tors.	209	—	162	-47	184	-25
16		CH ₂ asym. str.	2945	2983	2972	+27	2974	+29
17		CH ₃ asym. def.	1444	1450	1446	+2	1450	+6
18		CH ₃ rock	1079	1058	1025	-54	1086	+7
19		CH ₂ twist	890	887	936	+46	953	+63
20	B1	skel. oop	429	391	421	-8	441	+12
21		CH ₃ tors.	239	—	172	-67	201	-38
22		CH ₂ str.	3086	2085(A1)	3109	+23	3101	+15
23		CH ₃ asym. str.	2972	2996	2971	-1	2975	+3
24		CH ₃ sym. str.	2893	2893	2881	-12	2882	-11
25		CH ₃ asym. def.	1458	1461	1538	+80	1441	-17
26		CH ₃ sym. def.	1386	1383	1441	+55	1416	+30
27		CH ₂ rock	1282	1278	1273	-9	1273	-7
28		CH ₃ rock	996	1141	973	-23	986	-16
29		C—C str.	974	970	935	-39	928	-47
30		C=C—C bend	435	(431)	414	+21	378	-57
		rms				40.7		27.9
		max.				-117		+63

^a All results are gas phase unless stated otherwise.^b MM results compared to ref. 8.

the MM4 values, although less so for the *gauche*-conformer.

Some *cis*- and *skew*-1-butene frequencies are difficult to assign, since so many modes are coupled together. This is especially true for CH₂/CH₃ deformations are rocking frequencies. For *cis*-1-butene, the MM4 rms difference from experiment is calculated to be 37 cm⁻¹, but this is reduced to 28 cm⁻¹ if the scaled *ab initio* values for frequencies 18–20 are substituted for experimental ones. Frequency 20 for *skew*-1-butene is calculated far from experiment by MM but closer to *ab initio*. Similarly, the *skew*-1-butene rms is calculated to be 32 cm⁻¹ from experiment but is reduced to 25 cm⁻¹ if experimental frequencies 18–20 are substituted with the scaled *ab initio* values.

Durig and co-workers published IR/Raman vibrational frequencies for *cis*- and *gauche*-3-methyl-1-butene.¹⁸ Although most of their assignments agree with the MM results, there are some problems. Durig and co-workers report an extra CH₃ symmetric stretch frequency at 2891 and 2875 cm⁻¹ for the *cis*- and *skew*-conformers, respectively. Furthermore, a CH out-of-plane deformation (frequency 19 in Tables XI and XII in the Supplementary Material) is not assigned at all. Thus, *ab initio* calculations at the HF/6-31G** level were carried out in order to resolve discrepancies between MM4 and experiment.

MM4 methyl symmetric deformations 17/18 for *cis*- and *skew*-3-methyl-1-butene are both calculated +28/+40 cm⁻¹ and +61/+77 cm⁻¹ higher

TABLE IX.
skew-1-Butene (C₄).^a

	Mode	Exp. ¹⁷	Exp. ⁹	<i>Ab initio</i> ^c	Δ	MM3	Δ^b	MM4	Δ^b
1	=CH ₂ asym. str.	3090	3090	3047	-43	3107	-17	3100	+10
2	CH str.	3019	3018	2977	-42	3040	+21	3041	+22
3	=CH ₂ sym. str.	3008	2993	2963	-45	3009	+1	3017	+9
4	CH ₃ asym. str.	2982	2980	2930	-50	2968	-14	2970	-12
5	"	2978	2980	2922	-58	2968	-10	2968	-10
6	CH ₂ asym. str.	2948	2936	2894	-42	2930	-18	2934	-14
7	CH ₃ sym. str.	2936	2904	2862	-42	2900	-36	2886	-50
8	CH ₂ sym. str.	2888	2886	2854	-32	2871	-17	2873	-15
9	C=C str.	1647	1641	1688	+41	1678	+31	1666	+19
10	CH ₃ asym. def.	1469	1468	1472	+3	1460	-9	1450	-19
11	CH ₃ sym. def.	1463	1459	1463	0	1456	-7	1447	-16
12	CH ₂ bend	1444	1439	1453	+9	1443	-1	1414	-30
13	=CH ₂ in-pl. bend	1421	1414	1425	+4	1493	+72	1489	+68
14	CH ₃ sym. def.	1380	1378	1391	+11	1406	+26	1408	+28
15	CH ₂ wag	1318	1316	1330	+12	1353	+35	1349	+31
16	HC=CH in-pl. bend	1296	1294	1288	-8	1243	-53	1301	+5
17	CH ₂ twist	1264	1262	1261	-3	1190	-74	1263	-1
18	CH ₃ rock	1177	1028	1171	-6	1129	-48	1174	-3
19	CH ₃ out-of-pl. rock	1128	887	1076	-52	1020	-108	1058	-70
20	=CH ₂ in-pl. rock	1079	1175	1023	-56	1006	-73	974	-97
21	C—C str.	1020	1076	985	-35	988	-32	1003	-17
22	HC=CH op. wag	993	998	959	-34	1080	+87	1021	+28
23	=CH ₂ out-of-pl. wag	912	910	962	+50	968	+56	957	+45
24	C—C stretch	854	855	825	-29	888	+34	857	+3
25	CH ₂ rock	784	796	770	-14	812	+28	783	-1
26	=CH ₂ twist	634	631	636	+2	608	-26	615	-19
27	C=C—C bend	439	—	417	-22	418	-21	427	+12
28	C—C—C bend	301	—	307	+6	321	+20	311	+10
29	CH ₃ tors.	—	—	225	—	243	—	266	—
30	=C—C tors.	103	—	103	0	100	-3	96	-7
			rms			43.1 ^d / 37.0 ^e		32.3 ^d / 25.3 ^e	
			max.			-108 ^d / +87 ^e		-97 ^d / +68 ^e	

^a All results are gas phase unless stated otherwise.^b MM results compared to ref. 17.^c HF / 6-31G** frequencies are scaled by a factor of 0.9.^d rms compared only to experimental frequencies.^e rms compared with experiment except for frequencies 18, 19, and 20, which are compared to *ab initio*.

than experiment, respectively (See Tables XI and XII, Supplementary Material). The *ab initio* differences are smaller, with +11 / -8 cm⁻¹ differences for *cis*- and +46 / +27 cm⁻¹ deviations for *skew*-3-methyl-1-butene. The =CH₂ rock and wag frequencies (25 and 30) are assigned much higher and lower, respectively, than *ab initio* and MM4. Experimental frequencies 32 and 33 for *skew*-3-methyl-1-butene appear close to MM4 and *ab initio*, but for the *cis*-conformer these same experimental frequencies are more than 100 cm⁻¹ lower than either the *ab initio* or MM4 results. For *skew*-3-methyl-1-

butene, some of the *ab initio* skeletal bending and methyl torsion frequencies agree better with the MM4 results than the experimental ones.

For *cis*-3-methyl-1-butene, the overall rms error between experiment and MM4 is 39 cm⁻¹, and for the *skew*-conformer it is 35 cm⁻¹. The rms errors calculated with *ab initio* results substituted for some of the aforementioned experimental problem frequencies are also presented. When scaled *ab initio* frequencies 18, 19, 25, 26, 32, and 33 are substituted for experiment, the rms value becomes 27 cm⁻¹ for *cis*-3-methyl-1-butene. For *skew*-3-

TABLE XIII.
***cis*-2-Butene.^a**

Sym.	Mode	Exp. ⁸	Exp. ⁹	HF/6-31G** (Scaled)	MM3	Δ^b	MM4	Δ^b
A1	CH str.	3034	3035	3319 (2987)	3031	-3	3024	-10
B1	"	3030	3052	3292 (2963)	3017	-13	2993	-37
A1	CH ₃ str.	2979	2930	3289 (2960)	2999	+20	3003	+24
B1	"	2979	2992	3268 (2941)	2990	+11	3002	+23
A2	"	2979	2988	3222 (2900)	2969	-10	2971	-8
B2	"	2979	2948	3221 (2899)	2969	-10	2970	-9
A1	"	2931	2902	3178 (2860)	2889	-42	2890	-41
B1	"	—	2894	3175 (2858)	2886	-8	2887	-7
A1	C=C str.	1669	1668	1904 (1714)	1714	+45	1691	+22
B2	CH ₃ def.	1462	1458	1625 (1463)	1552	+90	1449	-13
A2	"	1462	1454	1618 (1456)	1450	-12	1445	-17
A1	"	1462	1464	1615 (1454)	1446	-16	1441	-21
B1	"	1462	1444	1610 (1449)	1458	-4	1430	-32
B1	CH rock	1422	1422	1575 (1418)	1441	+19	1484	+62
A1	CH ₃ def.	1389	1384	1556 (1440)	1403	+14	1410	+21
B1	"	1397	1408	1515 (1364)	1368	-29	1385	-12
A1	CH rock	1267	1268	1399 (1259)	1270	+3	1273	+6
B1	CH ₃ rock	1134	1134	1258 (1132)	1089	-45	1135	+1
A2	CH wag	1044	1050	1176 (1058)	1101	+57	1066	+22
B2	CH ₃ rock	1016	1037	1169 (1052)	968	-48	1042	+26
A1	"	1009	1010	1112 (1001)	1032	+23	1045	+36
B1	C—C str.	978	971	1110 (999)	962	-16	979	+1
A2	CH ₃ rock	—	950	1042 (938)	952	+2	971	+21
A1	C-C str.	881	864	922 (830)	862	-19	881	0
B2	CH wag	685	685	768 (691)	726	+41	733	+48
B1	C=C-C bend	581	566	608 (548)	535	-46	533	-48
A2	sym. def. oop	402	396	431 (388)	422	+20	429	+27
A1	C=C—C bend	304	258	310 (279)	295	-9	304	0
B2	CH ₃ tors.	—	—	136 (122)	133		146	
A2	"	—	—	133 (120)	102		101	
		rms				31.4		26.4
		max.				+90		+62

^a All results are gas phase unless stated otherwise.^b MM results compared to ref. 8.

methyl-1-butene, substituting experimental frequencies 18 and 19 with scaled *ab initio* results gives an rms of 33 cm⁻¹. The MM3 results are actually very close to the MM4 ones. Again, there is quite a bit of coupling between the vibrational modes for these molecules, and deciding on assignments for each frequency was difficult.

2-Butene

Both the *cis*- and *trans*-2-butene spectra are improved with MM4 compared to MM3. The results are presented in Tables XIII and XIV. *Ab initio*

calculations at the HF/6-31G** level are included for comparison.

1,4-Cyclohexadiene

The infrared and Raman spectra of 1,4-cyclohexadiene were reported in the liquid phase by Stidham (see Table XV in Supplementary Material).¹⁹ The MM4 assignments for frequencies 14–16 and 21–22 do not agree with experiment. Thus, a HF/6-31G** calculation was carried out to help clarify these assignments. *Ab initio* frequencies 14–15 and 21–22, which are ring stretching

TABLE XIV.
***trans*-2-Butene.^a**

Sym.	Mode	Exp. ⁸	Exp. ⁹	HF/6-31G** (Scaled)	MM3	Δ^b	MM4	Δ^b
Ag	CH str.	3011	3011	3298 (2968)	3046	+35	3041	+30
Bu	"	3036	3021	3293 (2964)	3039	+3	3035	-1
Ag	CH ₃ str.	2954	2965	3254 (2929)	2972	+18	2976	+22
Bu	"	2976	2960	3251 (2926)	2972	-4	2976	0
Au	"	2948	2960	3220 (2898)	2970	+22	2973	+25
Bg	"	2950	2965	3220 (2898)	2970	-20	2972	+22
Ag	"	2930	2926	3171 (2854)	2880	-50	2881	-49
Bu	"	2892	—	3170 (2853)	2879	-13	2881	-11
Ag	C=C str.	1680	1681	1913 (1722)	1734	+54	1703	+23
Bu	CH ₃ def.	1455	1449	1625 (1463)	1475	+20	1441	-14
Au	"	1444	1471	1619 (1457)	1444	0	1438	-6
Bg	"	1457	1455	1608 (1447)	1444	-13	1438	-19
Ag	"	1457	1455	1608 (1447)	1443	-14	1428	-29
Bu	"	1379	1393	1553 (1398)	1440	+61	1397	+18
Ag	"	1385	1389	1550 (1395)	1380	-5	1390	+5
Bu	CH wag	1306	1311	1447 (1302)	1345	+39	1344	+38
Ag	CH wag	1309	1309	1447 (1302)	1230	-79	1313	+4
Ag	CH ₃ rock	1138	1145	1263 (1137)	1072	-66	1146	+8
Bu	C—C str.	1069	1072	1180 (1062)	1133	+64	1067	-2
Bg	"	1043	1043	1171 (1054)	1041	-2	1060	+17
Au	"	1024	1057	1144 (1030)	1012	-12	1047	+23
Au	CH ₃ wag	975	964	1065 (959)	957	-18	995	+20
Bu	"	966	980	1105 (995)	963	-3	1004	+38
Ag	C—C str.	864	870	937 (843)	887	+23	899	+35
Bg	CH wag	750	746	836 (752)	810	+60	779	+29
Ag	S. def.	501	507	535 (482)	460	-41	472	-29
Bu	"	290	—	304 (274)	292	+2	296	+6
Au	"	240	—	265 (234)	239	-1	250	+10
Bg	CH ₃ tors.	210	—	237 (213)	205	-5	217	+7
Au	—	—	—	185 (167)	156	—	167	—
		rms				34.8		22.4
		max.				-79		-49

^a All results are gas phase unless stated otherwise.^b MM results compared to ref. 8.

and in-plane H—C=C—H bending modes, respectively, do not agree with experiment and are much closer to the MM4 (and MM3) assignments. The MM4 CH₂ wagging frequencies are calculated about 170 cm⁻¹ higher than experiment and *ab initio*. The C_{sp²}—C_{sp³}—H (atom type 2-1-5) bending constant affects this frequency the most and could be lowered to improve the agreement with experiment. However, this constant also affects the CH₃ rocking frequencies for isobutene (no.'s 8, 13, 18, and 28 in Table VIII) and *trans*-isoprene (no.'s 18 and 19 in Table XX), which would be calculated too low if this constant was reduced. Perhaps still more off-diagonal terms are needed to calculate the highly coupled vibrational modes of 1,4-

cyclohexadiene. The rms differences from experiment (without frequencies 14–15 and 21–22) are 62 cm⁻¹ for MM3 and 46.7 cm⁻¹ for MM4.

Cyclopentene

MM3 parameters for five-membered rings were not determined using vibrational frequency evaluations, but rather most of the open-chain force parameters were carried over. Thus, the MM4 force constants for five-membered rings were evaluated from the beginning. This involved assigning new atom types for C_{sp²} (type 122) and C_{sp³} (type 123) to these atoms when they were contained in a

TABLE XVII.
***trans*-1,3-Butadiene.^a**

Sym.	Mode	Exp. ²⁶	Exp. ²⁷	MM3	Δ^b	MM4	Δ^b
A _g	CH ₂ stretch	3101	3105	3108	+4	3101	0
	CH stretch	3014	3025	3034	+10	3036	+22
	CH ₂ stretch	3014	3014	3010	-4	3013	-1
	C=C stretch	1643	1644	1701	+58	1633	-10
	CH ₂ scissor	1442	1441	1474	+32	1462	+20
	CH rock	1291	1279	1213	-78	1305	+14
	C—C stretch	1205	1206	1185	-20	1195	-10
	CH ₂ rock	890	887	883	-7	860	-30
	C=C—C bend	513	513	507	-6	509	-4
A _u	C-H wag	1013	1022	1101	+88	1000	-13
	CH ₂ wag	908	905	955	+47	930	+22
	CH ₂ twist	524	535	508	-16	532	+8
	C-C tors.	163	163	164	+1	148	-15
B _u	CH ₂ stretch	3102	3103	3108	+1	3101	-1
	CH stretch	3056	3062	3037	-19	3035	-21
	CH ₂ stretch	3010	2986	3009	-1	3014	+4
	C=C stretch	1599	1597	1569	-30	1591	-8
	CH ₂ scissor	1385	1381	1396	+14	1409	+24
	C-H rock	1296	1297	1253	-43	1337	+41
	CH ₂ rock	991	988	1033	+42	1014	+23
	C=C—C bend	301	301	364	+63	337	+36
B _g	C-H wag	967	974	1090	+123	943	-24
	CH ₂ wag	911	908	956	+45	929	+18
	CH ₂ twist	753	754	661	-92	692	-61
	rms				48.3		22.7
	max.				+116		+61

^a All results are gas phase unless stated otherwise.^b MM results are compared to those in ref. 26.

five-membered ring. Frequencies for cyclopentene and cyclopentadiene have been examined using experimental frequencies in combination with *ab initio* results to verify the experiment and reassign ambiguous frequencies. It was found that frequencies were calculated better for five-membered rings without the bend-torsion-bend and stretch-stretch equations that are important in other systems. Accordingly, the corresponding constants were set to zero.

Two sets of experimental results exist for cyclopentene, as shown in Table XVI (see Supplementary Material).^{21,22} Discrepancies exist in the assignments for some of the cyclopentene frequencies. The C—H in-plane bend (frequency 13) and α , β -CH₂ wags (frequencies 15 and 16) are coupled to each other, making it ambiguous to assign a particular mode to a vibrational frequency. In the two IR experiments, the frequencies corresponding to α -CH₂ twists (frequencies 18 and 20), a β -CH₂ rock (frequency 28), and a ring bending (frequency 31) also had relatively large discrepan-

cies. In 1992 Allen and co-workers published *ab initio* results²³ using a DZ(d) basis set at the self-consistent field (SCF) theory with scaling by the SQM method of Pulay.²⁴ These computed frequencies helped to confirm the experimental assignments and cast doubt on those which deviate significantly from the *ab initio* calculations. In fact, Allen et al. reinterpreted the Villarreal and co-workers assignments for frequencies 15, 20, and 31 (see Table XII) from the original spectrum published in the dissertation of Villarreal.²⁵ All MM4 frequencies are compared mainly to the experimental frequencies in ref. 21, which in general (with the exception of frequency 28) agree more closely with the *ab initio* results.

Butadiene

The significant reductions in the rms errors for *trans*- and *cis*-butadiene are due to the uncoupling of the CH and CH₂ rocking and wagging frequen-

TABLE XVIII.
cis-1,3-Butadiene.^a

	Sym.	Mode	Exp. ²⁷	Exp. ²⁸	MM3	Δ^b	MM4	Δ^b
1	A ₁	CH ₂ stretch	3103	3088	3120	+17	3113	+10
2	B ₁	CH ₂ stretch	3103	3095	3116	+13	3109	+6
3	A ₁	C—H stretch	3039	3007	3035	-4	3037	-2
4	B ₁	C—H stretch	3039	3054	3030	-9	3033	-6
5	A ₁	CH ₂ stretch	3014	2992	3017	+3	3005	-9
6	B ₁	CH ₂ stretch	3014	2984	3012	-2	2994	-20
7	B ₁	C=C stretch	1633	1612	1670	+37	1671	+38
8	A ₁	C=C stretch	1612	1632	1618	+6	1584	-28
9	A ₁	CH ₂ scissors	1425	1425	1495	+70	1456	+31
10	B ₁	CH ₂ scissors	1403	1402	1450	+47	1465	+62
11	A ₁	C—H rock	—	1299	1287	-12	1350	+51
12	B ₁	C—H rock	—	1277	1203	-74	1296	+19
13	A ₁	CH ₂ rock	—	1075	1099	+24	1096	+21
14	B ₁	CH ₂ rock	1087	1085	1051	-36	1071	-16
15	B ₂	C—H wag	996	995	1045	+49	958	-38
16	A ₂	C-H wag	983	1032	1094	+111	937	-46
17	B ₂	CH ₂ wag	914	913	956	+42	934	+20
18	A ₂	CH ₂ wag	915	915	962	+47	925	+10
19	A ₁	C—C stretch	—	899	846	-53	844	-55
20	A ₂	C=C twist	727	742	663	-64	683	-44
21	B ₁	C=C-C bend	596	595	598	+2	582	-14
22	B ₂	C=C twist	468	475	473	+5	511	+43
23	A ₁	C=C-C bend	—	—	354	—	332	—
24	A ₂	C—C tors. ^c	—	136	86	—	-37	—
rms						43.8		31.9
max.						+111		+62

^a All results are gas phase unless stated otherwise.^b MM results compared to ref. 27, except for frequencies 11–13 which are compared to ref. 28.^c Frequency 24 is not included in the rms.

cies. As in benzene (Table II), the torsion-improper torsion-improper torsion term helped improve these frequencies. The results are presented in Tables XVII and XVIII.

Isoprene

Once again, the out-of-plane bending frequencies are improved in MM4 compared to MM3 for *trans*- and *gauche*-isoprene. The CH wagging and =CH₂ wagging/rocking frequencies are calculated closer to experiment by MM4 (see Tables XIX and XX in Supplementary Material).

Toluene

The same terms that improved benzene and styrene also affect toluene, including the

stretch–stretch and torsion-improper torsion-improper torsion terms. Thus, toluene is calculated closer to experiment by MM4 than MM3, as shown in Table XXI (see Supplementary Material).

Cyclopentadiene

Experimental gas phase IR³¹ and calculated (multiconfiguration self-consistent field (MCSCF))³² vibrational frequencies are available for cyclopentadiene. The calculated frequencies were not scaled by the authors. The major discrepancies come from the ring deformation and torsion frequencies. Attempting to improve these frequencies by increasing bending force constants or changing torsional parameters comes at the expense of structural and energy data involving five-membered ring structures with the same parameters. Also, the CH

TABLE XXIII.
Comparison of MM3 and MM4 RMS Differences from Experiment for Alkenes.

	MM3		MM4	
	rms	Max. Error	rms	Max. Error
Ethylene	68.2	+124	16.7	-41
Propene	28.3	-72	17.8	-51
Isobutene	40.7	-117	27.9	+62
<i>cis</i> -2-Butene	31.4	+90	26.4	+62
<i>trans</i> -2-Butene	34.8	-79	22.4	-49
<i>skew</i> -1-Butene	37.0	+87	25.3	+68
<i>cis</i> -1-Butene	(38.2)	(+87)	(28.3)	(-69)
<i>cis</i> -3-Methyl-1-butene	36.1	+100	27.4	+66
<i>skew</i> -3-Methyl-1-butene	(35.9)	(+83)	(33.0)	(+75)
1,4-Cyclohexadiene	(61.8)	(-156)	(46.7)	(+175)
Cyclopentene	(47.2)	(+116)	(32.0)	(-72)
Overall^a	38.2	+124	24.7	+68

^a The *cis*-1-butene, *gauche*-3-methyl-1-butene (the second lowest energy structures), 1,4-cyclohexadiene, and cyclopentene results (all given in parentheses) are not included in the overall errors due to ambiguities in the frequency assignments.

out-of-plane bending frequencies are calculated lower than experiment, as usually occurs for conjugated hydrocarbons with MM4. The results are shown in Table XXII (Supplementary Material).

Conclusions

In addition to the data presented here, a few additional compounds have been studied and are tabulated in the Supplementary Material. These are *cis*-1-butene, *cis*-3-methyl-1-butene and the *gauche* conformation of the same molecule, 1,4-cyclohexadiene, cyclopentene, *trans*- and *gauche*-isoprene, toluene, and cyclopentadiene.

A summary of the results for alkenes is given in Table XXIII. Of the seven structures examined herein, the largest error in frequency obtained with MM3 and 124 cm⁻¹, and this was reduced to 68 cm⁻¹ with MM4. The corresponding root mean square errors were 38 and 25 cm⁻¹. With the conjugated hydrocarbons (Table XXIV), the largest and rms errors with MM3 over eight compounds were 129 and 52 cm⁻¹ if the benzene B_{2u} CC stretching frequency was omitted, and the corresponding numbers with MM4 were -100 and 31 cm⁻¹.

As was mentioned earlier in the alkanes work,² the improvements here do not result from many

TABLE XXIV.
Comparison of MM3 and MM4 rms Differences from Experiment for Conjugated Hydrocarbons.

	MM3		MM4	
	rms	Max. Error	rms	Max. Error
Benzene	57.9 ^a (85.3)	+129 ^a (+348)	33.6	-89
Styrene	55.7	+115	29.6	+83
<i>trans</i> -Butadiene	47.1	+116	22.7	-62
<i>cis</i> -Butadiene	43.8	+111	31.9	+62
<i>trans</i> -Isoprene	48.6	-129	26.1	-58
<i>gauche</i> -Isoprene	49.0	-168	30.1	+74
Toluene	50.6	+109	30.5	-100
Cyclopentadiene	54.0	+107	38.6	-99
Overall	51.5^a	+129^a	31.4	-100

^a Values without benzene B_{2u} C—C stretching frequency (with the B_{2u} frequency included, the overall rms / max. values are increased to 55.6 / +348 cm⁻¹).

small improvements but rather from a few discreet but significant improvements. Therefore, while the rms improvement may not appear dramatic, the actual improvements in the calculated spectra tend to be significant.

Several explicit off-diagonal terms have been added into the MM4 calculations which were not included in MM3. In each case they have improved the accuracy of the calculation in a significant way. But also in most cases, these elements tend to introduce adverse effects into other parts of the calculation, particularly the torsional barriers and the heats of formation. It is therefore important to decide how much error one is willing to accept and where one wants those errors to occur. In general, we have taken much of the error in the higher vibrational frequencies. The low frequencies are important in determining thermodynamic quantities, so we have tried to fit those rather well. The higher frequencies normally have little effect on structure, thermodynamics, or anything else that we have examined, so that seems like the best place to take the errors. Other important quantities which are perhaps not fit well include the cis/gauche butadiene relationship and the rotational barriers about double bonds versus their geometries. In our view, the experimental/*ab initio* situation here is less than completely convincing, so we are unwilling to force fit to data that we are not confident are correct.

The alkenes and conjugated hydrocarbons are to some extent affected by hyperconjugation. The results reported in these and preceding articles have taken hyperconjugation into account, although the subject has not yet been dealt with in full detail. That subject will be taken up in the following manuscript.⁵

Supplementary Material

The package of Supplementary Material referred to in the text (nine tables of vibrational spectra) is available from the authors upon request.

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